

Interactive comment on “Photochemical mineralisation in a humic boreal lake: temporal variability and contribution to carbon dioxide production” by M. M. Groeneveld et al.

Anonymous Referee #1

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Overview

In this manuscript, Groeneveld et al. investigated the photochemical production of carbon dioxide in a humic boreal lake of Sweden. The study presents new data on the temporal (monthly) variability of apparent quantum yields (AQY) for the photoproduction of DIC, and on the temporal variability of calculated DIC photoproduction rates for this lake. The study concludes that future studies need to better incorporate the temporal variability of AQY DIC when making synoptic estimates of DIC photoproduction, and also concludes that DIC photoproduction is a minor contributor to CO₂ fluxes from lakes. The findings are largely non-controversial but they contribute to a growing

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body of evidence supporting these conclusions. The topic and scientific contribution are adequate for Biogeosciences. The writing style is generally good and the results are new, the methods to calculate the AQY and photochemical rates are sound, and the manuscript has potential for publication in Biogeosciences. The authors validated their calculated rates against rates measured in situ using an experimental setup, which is a nice addition. That said, there are some major concerns that need to be properly addressed and some major improvements are needed. I recommend the manuscript for publication only after the following concerns have been addressed.

Major Comments

1. Temporal variability of the AQY: Too little is done to assess if the difference between AQY is significant beyond the uncertainty of the measurements. The authors need to provide some measure of the uncertainty in the calculated AQY and they need to demonstrate using statistics that the month-to-month variability is significant beyond the uncertainty bounds of the AQY calculations. Uncertainty bounds around the coefficients (m_1 , m_2) need to be included. This is particularly important here because the temporal variability of the AQY is at the core of this study. Furthermore, in the text the authors go back and forth on whether the difference between AQY is important or not, and this more rigorous assessment would help. Also, instead of a single figure 1b showcasing all AQY at once, I would suggest creating a 6-panel figure with each panel showcasing a single AQY with its 90% confidence interval (one panel for each month). In each panel, the showcased spectra and its confidence interval would be in color and the other months' spectra would be shown as gray curves in the background, and the pooled AQY as a black curve. In addition to the statistics, this figure would help visualizing how uncertainties and temporal variability compare.

2. Use of Supor filters: In my experience, Supor Polyethersulfone filters strongly adsorb humic material, and can lead to a large decrease in the CDOM (effects were quite

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severe on the river waters that I have tested in the past). I would expect the problem to be exacerbated for water from humic lakes. I am therefore a little concerned about the effects of using these filters on the overall results from this manuscript. Ideally, the authors should try to assess and report the extent of the problem (in supplementary material and in main text) by comparing the effects of these filters with that of other, more adequate, types of membrane such as polycarbonate or nylon membrane. This is important here because this has potentially some important consequences for the findings of this study and can contribute to the AQY quantum yield and in the modeled DIC photoproduction rates.

3. Lag between irradiance and DIC photoproduction when using the monthly measured AQY (abstract and discussion): This argument does not make sense to me. I do not understand how the apparent lag between modeled irradiance and calculated DIC photoproduction rates (when using monthly AQY) suggests that AQY spectra change on time scales shorter than a month. This needs to be more clearly explained, or reassessed. Second, the lag in the data mentioned by the authors is not clearly seen in the data (mostly because figure 3 and S3 are not very clear). The authors mentioned they used a cross-correlation function that suggested a lag of 2-3 week lag. The cross-correlation function needs to be shown in the body of the manuscript (if the argument about the lag holds somehow).

4. New figure: I would strongly encourage the authors to add a new figure showing the location of the lake on a map of Sweden, which could be combined with Figure S2, which I think would also benefit from being shown in the main body. This would be a figure linked to the methods and that would help the reader get a sense of the study area and experiment setup.

5. Contribution to CO₂ fluxes (Page 17140, lines 24-28): The authors compared their calculated DIC photoproduction rates to CO₂ fluxes estimates that are referenced as unpublished data. If these numbers are presented, the methods and data for estimating the CO₂ fluxes should be presented as well.

Minor comments

- Figure 1a: In general, CDOM absorbance data below 240 nm are not reliable so I would suggest to only show the spectra from 250 to 600 nm, or even from 290 -600 nm since the data are not used below 290 nm and the spectral ranges of the CDOM spectra would match the displayed AQY.
- Figure 3 (and S3): The large number of symbols shown on the figure make it difficult to see the patterns. I would suggest using continuous lines instead, and separate the integrated irradiance and DIC production into two panels (top and bottom). The current figure is a little muddled and not much besides the seasonal variability can be seen.
- Abstract (line 15) (and throughout manuscript): Use “between” or “among” instead of “across”.
- page 17129 (line 18): SUVA is not a “measure” of aromaticity. The word “indicator” would be more appropriate.
- Equation (3): need to change “alpha” to “a”
- page 17136 (line 9) (and throughout): Please make sure P is defined,..I would suggest using “p-value” instead of P to prevent ambiguity.
- page 17136 (line 20): The change mentioned here might be significant but is smaller than the change in production. Avoid using “significant” here as it implies the change is significantly larger than the uncertainty.
- page 17136 (line 21): remove "were similar",...not sure what is meant here and contrary to the statement they are increasing.
- page 17138 (line 20): The in situ rates could be calculated for the depth interval corresponding to the submerged tube. I suggest removing this statement.
- Page 17139 (line 10): “relatively more DIC produced”,...confusing,..consider changing wording

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